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RAPID COMMUNICATION

Observation of blue shifts in ZnO/ZnMgO multiple quantum well structures by ion-implantation induced intermixing

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Abstract

Implantation with low-energy (80 keV) oxygen ions and subsequent rapid thermal annealing at 800 °C are used to induce intermixing in a stack of 19 ZnO/Zn\(_{0.7}\)Mg\(_{0.3}\)O multiple quantum wells grown on sapphire by molecular beam epitaxy. Large blue shifts of more than 300 meV have been observed for doses up to \(1 \times 10^{16} \text{ cm}^{-2}\), with no observation of saturation. This process is driven by the creation of defects by implantation which encourage the diffusion of Mg from the barrier layers into the ZnO quantum wells. Although defects are introduced during the implantation process, good recovery of the cathodoluminescence is seen following rapid thermal annealing. The Zn–Mg interdiffusion in this system has also been calculated for the corresponding ion doses, and the diffusion coefficient extracted. This study has significant implications for band gap engineering of ZnO/ZnMgO optoelectronic devices.

ZnO is a semiconductor with a wide band gap of 3.4 eV and large exciton binding energy of 60 meV at room temperature. When coupled with recent advances in both single crystal and epitaxial growth technology [1], these electronic characteristics make ZnO a strong candidate for a range of blue and UV optoelectronic devices [2]. The issue of making p-type ZnO, which has until now limited device development, is coming closer to being resolved, with the first reports of electroluminescence from epitaxial ZnO homojunctions emerging [3]. As ZnO devices are realized, band gap engineering of the system will become increasingly important for the creation of monolithic devices. Such devices could be used for a variety of applications including UV detectors (for fine tuning UV bands in the UVA and B regions), ultra high density data storage systems where two laser diodes active in the UV region could be used for dual layer DVD reading and writing, tuning the emission of ZnO devices to directly match that of a phosphor for use in lighting applications, and tuning the emission wavelength for specific bio-molecular applications.

Alloying ZnO with CdO [4, 5] and MgO [6–8] are proven technologies for respectively red- or blue-shifting the emission wavelength. Blue-shifting the emission has been fine-tuned by changing the Mg composition of the layer [7, 8] or by inducing thermal intermixing in ZnMgO superlattices by annealing for 1 h [9, 10]. These techniques both result in wavelength shifts throughout the whole material, which is a disadvantage when trying to achieve monolithic integration of devices with different functionality upon the same chip. Additionally, the large effective mass of carriers in ZnO means that amount of...
wavelength tuning achievable by adjustment of the quantum well widths in these systems is limited. Thus to fine-tune the band gap in both vertical and lateral directions, over a wide wavelength range, we must look toward different methods of precisely tuning the emission wavelength.

Several techniques currently exist that can achieve this goal including selective area epitaxy [11] and layer intermixing [12], including intermixing induced by ion implantation [13, 14]. Ion-implantation induced intermixing is advantageous for two reasons. Firstly, the amount of defects introduced can be precisely controlled (thus precisely controlling the amount of wavelength shifting) and, secondly, no further processing and regrowth is required. Also, the monolithic integration of devices by intermixing allows facet degradation issues to be overcome. In this work, low energy (80 keV) oxygen implantation into a ZnO/ZnMgO superlattice was conducted. 80 keV was chosen as the incident energy to place the peak of the damage across the quantum well region. Oxygen ions were chosen to avoid complications arising from introducing an impurity ion into the system. Subsequent rapid thermal annealing (RTA) at 800 °C for 60 s was employed to activate the intermixing process and recover the luminescence from the layers. To complement the experimental data, we have also conducted theoretical modelling of the implantation induced intermixing process in order to extract the values of the diffusion length of Mg in this system. The diffusion length provides a measure of the extent of the disordering introduced during ion implantation. To the best of our knowledge, at the time of publication this is the first work which both focuses on intermixing studies in the ZnO/ZnMgO system, and provides theoretical determination of the Mg diffusion length.

The sample used in this experiment was a single crystal stack of 19 ZnO/Zn0.7Mg0.3O multiple quantum wells (MQWs) grown on a-plane sapphire by molecular beam epitaxy. Details of the growth conditions can be found elsewhere [10]. The sample consisted of a 10 nm ZnO buffer grown at low temperature (250 °C), followed by a 500 nm thick ZnO layer grown at 500 °C. The 19 ZnO/Zn0.7Mg0.3O MQWs were grown on top of these buffers. The ZnO wells were 2 nm thick, and the Zn0.7Mg0.3O barrier layers were 5.5 nm thick. The multiple quantum wells are capped by a 50 nm layer of Zn0.7Mg0.3O.

Prior to all experiments, the sample was cut and chemically cleaned. Some pieces of the sample were reserved for an annealing study. The rest were implanted with 80 keV O− in the dose range of 5 × 10^{14}−1 × 10^{16} cm−2 at room temperature, using a 1.7 MV tandem accelerator (NEC, 5SDH-4). The ion beam flux was ∼3 × 10^{12} cm−2 s−1. During implantation, samples were tilted 7° relative to the incident beam to minimize channeling. A piece of Si was used to mask a part of the sample during implantation to be used as a reference. TRIM [15] code calculations were employed to calculate the displacement profile. Figure 1 shows the calculated displacement density expected during the implantation as a function of depth. Also shown in this figure is the location of the MQWs with respect to the displacement profile. Rapid thermal annealing of the samples (both implanted and unimplanted) was conducted at 800 °C in an Ar ambient for 60 s. One piece of sample was left as-grown for reference.

![Figure 1](https://example.com/figure1.png)

Following implantation and annealing, cathodoluminescence (CL) spectroscopy was performed at 77 K using an Oxford Instruments MonoCL2 system installed on a JEOL35C scanning electron microscope (SEM). The CL spectra were measured using a Hamamatsu R943-02 Peltier cooled photomultiplier tube and a 1200 lines/mm grating blazed at 500 nm. The SEM was operated at 5 keV to ensure that the primary excitation occurred mainly within the quantum well region. At this energy, most of the signal is generated at a depth of 40 nm with a maximum generation depth of 120 nm. This coincides well with the displacement profile across the quantum wells as shown in figure 1. The electron beam current was kept fixed at ∼30 nA. All CL spectra were corrected for system response.

Theoretical modelling of the interdiffusion was carried out to extract the Mg diffusion lengths, using a model described previously [16]. In this study, a five stack of ZnO/Zn1−xMgxO MQW was modelled. The well was nominally undoped, and the effect of impurities was ignored. The strain in the system arising from a small (~0.5% at 30% Mg content) lattice mismatch was considered negligible and the ZnMgO was assumed to be in the wurtzite phase. A finite well width of 2 nm corresponding to the width of the wells in the samples was used. The model also assumed that Fick’s second law of diffusion applies [17]; that is, an isotropic interdiffusion of Zn and Mg occurs with the diffusion being independent of the concentrations of the constituent elements. Equation (1), which gives the diffused Mg composition profile, \( w(z) \), across the QW can be used to calculate the diffusion length, \( L_d \) of Mg

\[
w(z) = w_0 \left\{ 1 - \frac{1}{2} \left[ \text{erf} \left( \frac{L_z + 2z}{4L_d} \right) + \text{erf} \left( \frac{L_z - 2z}{4L_d} \right) \right] \right\}
\]

where \( w_0 \) is the as-grown Mg fraction in the barrier, \( L_z \) is the as-grown width of the quantum well, \( z \) is both the
quantization and the growth axis (well is centred at $z = 0$), and $\text{erf}$ denotes the error function [16]. The error function is used to simulate the interdiffusion at the heterointerface by creating a more diffuse profile instead of a sharp step. From equation (1), the parameters for the interdiffused quantum well can be determined; however, some key parameters for the ZnO/ZnMgO system must first be known. These parameters include the energy band gap for Zn$_{1-x}$Mg$_x$O which is taken as $E_g = 3.37 + 2.51x$ [18] and the band offsets which are, $\Delta E_c/\Delta E_v = 70/30$ [19]. Due to a lack of available data for the MgO system, the MgO hole and electron masses have been assumed to be the same as for ZnO ($m_h/m_e = 0.28x + 0.28(1-x)$ and $m_{lh}/m_e = 0.8x + 0.8(1-x)$) [19]. This becomes important for large diffusion lengths, as at these values it is the most important factor in the determination of the wavefunction. Additionally, the excitonic contribution is assumed to be the same for all intermixed quantum wells.

Figure 2 shows CL spectra from the implanted and annealed samples. Note that a spectrum taken from the as-grown sample is shown for reference. This spectrum is the same as that from the unimplanted sample annealed at 800 °C for 60 s, which is not shown for clarity. This indicates that RTA alone is not sufficient to induce intermixing under these conditions. Some sample charging was evident during electron-irradiation in the SEM, resulting in varying intensities of the recorded spectra. Thus the spectra have been normalized to the ZnO peak of the as-received sample. The implanted samples all showed strong luminescence following implantation which was visible at room temperature, suggesting that any non-radiative defects introduced by ion implantation were mostly recovered during the RTA step. This is not surprising given the radiation hardness of ZnO [20]. It is evident from the CL spectra that the wavelength of the ZnO well ($\sim 3.4$ eV) blue shifts with increasing O ion dose toward that of the Zn$_{0.7}$Mg$_{0.3}$O peak located at $\sim 4$ eV. It is also useful to note that no significant increase in deep level emissions was seen following implantation and annealing.

The as-grown sample shows a narrow line-width, and a small shoulder on the low-energy side of the spectrum. The shoulder is part of the fine-structure of the ZnO excitonic peak and is most likely a phonon replica, which indicates that the material is of high quality. The ZnO peak becomes broader with increasing ion dose, and in fact for doses of $5 \times 10^{15}$ cm$^{-2}$ and $1 \times 10^{16}$ cm$^{-2}$, the spectra show a shoulder on the low-energy side. The broadening, as well as the shoulder feature, are most likely a result of an inhomogenous distribution of defects across the MQW region, leading to variations in the extent of intermixing across the region probed by CL. The calculated displacement density shown in figure 1 is supportive of this, as it shows that the displacement profile tails off significantly after about 100 nm. This could be overcome by conducting multiple-energy implants to create a uniform damage profile over the MQW region [21], or higher energy implants using the tail of the displacement distribution [14].

The magnitude of the blue shifts after RTA at 800 °C for 60 s as a function of implantation dose is shown in figure 3. It can be clearly seen that the energy shift (calculated as a shift from the as-received sample) increases with increasing dose without any indication of saturation. In this case, the energy shifts are driven by interdiffusion of Zn atoms from the wells diffusing into the barriers and Mg atoms from the barrier layers moving into the ZnO wells. This interdiffusion is made possible by the defects created during O ion implantation. Upon annealing, these defects become mobile and initiate the interdiffusion process. The oxygen introduced by implantation is effectively neutral in this system and does not contribute to the observed energy shifts.

The calculated values for the Mg diffusion length, $L_d$, as a function of implantation dose are also shown on this plot. These values represent the amount of disorder introduced into the system. They correlate very well with the calculated energy shifts, and further support the proportionality of the diffusion length (and hence disorder) to the implantation dose. Hence with ion implantation, the Mg profile around the quantum well is changing with increasing ion implantation dose. The implanted O ions introduce disorder into the system and cause...
Table 1. Calculated Mg diffusion coefficient, $D$, for the ZnO/Zn$_{1-x}$Mg$_x$O MQW structure implanted at various doses and annealed for 60 s at 800 °C.

<table>
<thead>
<tr>
<th>Dose (cm$^{-2}$)</th>
<th>Energy shift (eV)</th>
<th>$L_d$ (Å)</th>
<th>$D$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{14}$</td>
<td>0.058</td>
<td>5.7</td>
<td>$1.4 \times 10^{-17}$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>0.1186</td>
<td>9.8</td>
<td>$4.0 \times 10^{-17}$</td>
</tr>
<tr>
<td>$5 \times 10^{15}$</td>
<td>0.255</td>
<td>19.3</td>
<td>$1.6 \times 10^{-16}$</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>0.322</td>
<td>26.9</td>
<td>$3.0 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

Rapid Communication

both Mg and Zn to interdiffuse, creating a diffuse quantum well shape instead of an abrupt heterointerface. This is reflected in the $L_d$ values which follow the same trend as the energy shift. For the last point at a dose of $1 \times 10^{16}$ cm$^{-2}$, the calculated diffusion length varies a little from the trend. As mentioned previously, this is most likely due to the MgO electron and hole masses not being accurately known, which becomes significant for larger values of diffusion length. The inset of figure 3 shows the potential profile of five wells both before ($L_d = 0$ nm) and after ($L_d = 2.7$ nm) implantation with the highest dose of oxygen ions. It can be clearly seen that at this dose the quantum wells undergo almost complete intermixing.

Table 1 gives the values for the Mg diffusion coefficient, $D$, as a function of dose in this system implanted and annealed under the given conditions. The diffusion coefficient is related to the diffusion length by $L_d = 2\sqrt{Dt}$ where $t$ is the annealing time in seconds. The calculated Mg diffusion coefficients lie within the range $10^{-16}$–$10^{-17}$ cm$^2$ s$^{-1}$. These values compare well with the calculated bulk diffusivity of O in bulk ZnO, which has been determined to be $2.73 \times 10^{-17}$ cm$^2$ s$^{-1}$ at 850 °C [22]. The diffusion coefficients determined in our work increase with increasing implantation dose, reflecting the increase in defects in the system which enhance the Mg diffusivity. We were unable to find any data within the literature on Mg diffusion in ZnO, and thus our values could not be directly compared to previously determined values.

We have therefore shown that oxygen ion implantation and subsequent rapid thermal annealing can be used to fine-tune the band gap of a stack of 19 ZnO/Zn$_{0.7}$Mg$_{0.3}$O multiple quantum wells (2 nm thick). Large energy blue shifts of over 300 meV have been observed with no apparent saturation. The large energy shifts are a result of Mg–Zn interdiffusion induced by defect creation during ion implantation. The Mg diffusion lengths have been calculated for this system and correlate well with the experimental data. Cathodoluminescence data show that rapid thermal annealing at 800 °C enhances the diffusion process and removes most of the defects, allowing for good recovery in luminescence. The results of this study have significant implications for band gap engineering of ZnO/ZnMgO optoelectronic devices.

Acknowledgment

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References